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Monitoring Carbon Dioxide Sequestration in Deep Geological Formations for Inventory Verification and Carbon Credits

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Abstract

Large scale implementation of CO_2 Capture and Storage is under serious consideration by governments and industry around the world. The pressing need to find solutions to the CO_2 problem has spurred significant research and development in both CO_2 capture and storage technologies. Early technical success with the three existing CO_2 storage projects and over 30 years experience with CO_2-EOR have provided confidence that long term storage is possible in appropriately selected geological storage reservoirs. Monitoring is one of the key enabling technologies for CO_2 storage. It is expected to serve a number of purposes – from providing information about safety and environmental concerns, to inventory verification for national accounting of greenhouse gas emissions and carbon credit trading. This paper addresses a number of issues related specifically to monitoring for the purpose of inventory accounting and trading carbon credits. First, what information would be needed for the purpose of inventory verification and carbon trading credits? With what precision and detection levels should this information be provided? Second, what monitoring methods and approaches are available? Third, do the instruments and monitoring approaches available today have sufficient resolution and detection levels to meet these needs? Theoretical calculations and field measurements of CO_2 in both the subsurface and atmosphere are used to support the discussions presented here. Finally, outstanding issues and opportunities for improvement are identified.

Introduction

Geological storage of carbon dioxide, as a method to avoid atmospheric CO_2 emissions to the atmosphere, has been underway for more than a decade, beginning in 1996 with the Sleipner Project in Norway[1]. Today, more than 3 million tonnes of CO_2 are injected for the purpose of sequestration annually[1,2,3,4]. Another 30 million tonnes are injected for CO_2 enhanced oil recovery[5]. Many more sequestration projects are under development, with several new projects announced each year[6,7,8].

Growing interest in geological sequestration for avoiding or offsetting CO_2 emissions has stimulated the need to develop monitoring approaches for assuring that geological sequestration is safe and containment is effective[4,9,10,11]. Each of the three existing geological sequestration projects uses a different combination of monitoring techniques, depending on the questions that the monitoring program is trying to address, ease of access, and geological attributes of the site. For example, at Sleipner, a combination of time-lapse 2-D and 3-D imaging has been used to track migration of the injected CO_2 in the Utsira brine formation with great success[12]. Recently, gravity measurements were used to estimate the in situ density of CO_2 at Sleipner[13]. At Weyburn, a comprehensive program that included time-lapse 3-D seismic imaging, geochemical sampling and soil gas surveys was used as a multifaceted approach to demonstrate effective containment[14]. The In Salah Project plans to install a permanent 3-D seismic monitoring array, sample soil gases and introduce tracers for tracking CO_2 breakthrough into the gas reservoir[15].

In addition to these commercial-scale projects, monitoring methods have been tested on a smaller scale at pilot test sites[16,17,18]. Surface to borehole seismic imaging (VSP), cross-well seismic, cross-well EM, well logs (e.g. RST, resistivity), pressure transients, natural and introduced tracers, brine and gas composition sampling and analysis, flux accumulation chambers, soil gas sampling, and groundwater sampling have been used to monitor the fate and migration of CO_2 in the subsurface[16,17, 18, 19, 20].

Theoretical studies have also been carried out to identify additional monitoring technologies. Borehole gravity, surface EM, and self-potential have been evaluated for application to a Schraeder Bluff-like setting[21]. Pressure transients below secondary seals have been calculated[22]. Eddy covariance methods for monitoring surface fluxes have been assessed[23]. Open-path and plane- or satellite-based optical methods, including the potential for isotopic analysis, are also being developed[24,25].

As a result of experience with commercial-scale and pilot scale tests, together with theoretical studies, there is a high degree of confidence that methods are available for monitoring sequestration projects. In general, most of the monitoring methods have proved to be reliable and sensitive indicators of the fate of injected CO_2. However, in each case, methods were deployed, at least in part, for research and development purposes. Decisions regarding how they will be deployed on a routine basis have not yet been made. The rapidly growing number of sequestration projects and more extensive engagement with policy makers, investors and regulators—has stimulated the need to begin to assess which methods should be used, how frequently and with what precision.

In addressing these issues, the first question that must be asked is—what is the purpose for monitoring? Depending on who is asked, a different answer is provided. For example, site operators, environmental regulators and the public want to be assured that CO_2 sequestration is safe. Mineral right and surface right owners want to be assured that CO_2 is not migrating beyond site boundaries. Policy makers, carbon credit traders and investors want to be assured that CO_2 is not returning to the atmosphere. Reservoir engineers want information to calibrate and validate simulation models of CO_2 plume migration and predict long term containment. These are just a few of the evolving perspectives that will be brought to bear on the purposes for monitoring[9].

A number of studies have identified possible approaches for monitoring that would satisfy the needs outlined above[9, 11]. Methods span the gambit from 4-D seismic imaging to monitoring fluxes at the land surface; from remote sensing to ground water sampling. In fact, the tool box of potential monitoring methods is large. In many ways, the monitoring challenge is not to find methods that will work, but to find cost-effective approaches that are fit-for-purpose.

This paper deals specifically with monitoring approaches that are cost effective and suitable for inventory verification and carbon credit trading. Monitoring for potential ground water contamination, ecosystems impacts, human health and safety, and resource damage are not considered here. Certainly there will be overlaps in the information provided by any monitoring method, but identifying these is not the purpose here.

The accelerating pace of deployment of CCS, including the desire to obtain credits for avoided emissions, necessitates that we begin to converge on cost-effective monitoring protocols. Motivation here is to simplify this quest by addressing one of the most important purposes for monitoring, and perhaps the one that is most relevant in the international context of climate change mitigation.

To accomplish this, this paper sets out to address the following questions. First, what information would be needed for the purpose of inventory verification and carbon trading credits? With what precision and detection levels should this information be provided? Second, what monitoring methods and approaches are available? Third, do the instruments and monitoring approaches available today have sufficient resolution and detection levels to meet these needs? If not, what is needed to satisfy these needs?

These questions will be addressed in the context of a hypothetical storage project with an annual storage of 4 million tonnes per year, which is roughly equivalent to emissions from a 500 MW coal-fired power plant with capture and storage. To begin, recent international developments regarding inventory accounting will be reviewed to provide a context for the discussion.

Information Needed for Inventory Verification

The International Governmental Panel on Climate Change (IPCC) has recently issued two reports that have bearing on protocols for inventory verification[4,26]. In these, the CO_2 capture and storage chain is divided into the 4 systems shown in Figure 1:

1. Capture and compression;
2. Transport by pipeline or ship;
3. Injection system, including surface facilities such as the distribution pipelines and manifolds, measurement and control systems, wellheads, compression, pumps and injection wells; and
4. Geological storage reservoir.

Guidance for each of these systems has been provided. In each case, the system is considered as a CO_2 emission source.

Capture and Compression System

For capture and compression, the CO_2 source can be calculated from the difference between total emissions (determined by fuel consumption) and the metered amount that is transported for storage[26].

Pipeline System

Fugitive CO_2 emissions from pipelines can estimated based on “emissions factors” for natural gas pipelines[26]. This so-called Tier 1 methodology for reporting emissions does not require that measurements are actually made for emissions from the pipeline. Instead, they are estimated based on experience from other pipelines. The emission factor for pipelines has a range of 0.14 tonnes/year/km to14 tonnes/year/km, with a median value of 1.4 tonnes/year/km[26]. The uncertainty in these values is ± a factor of 2. Default emission factors are not available for ship transport, so actual losses would need to be measured at loading and unloading stations[26].

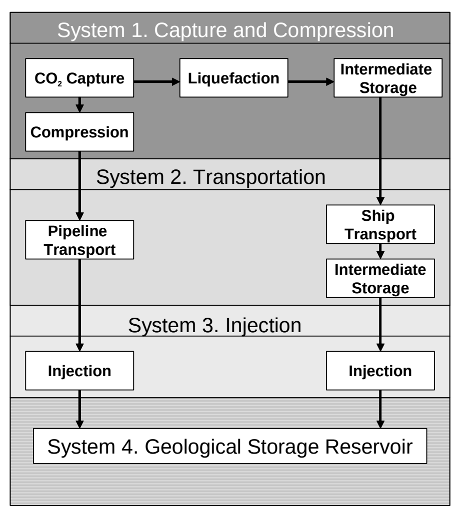

Figure 1. Schematic showing the 4 systems included in the CO_2 Capture and Storage inventory reporting guidelines (modified from ref. 26).

Injection System

The injection system includes surface facilities, distribution pipelines and manifolds, pumps, on-site compression and other ancillary equipment. The IPCC guidelines suggest it is good practice to directly measure the amount of CO_2 directly injected into the storage reservoir[26]. Methods are available to measure the quantity of injected CO_2 with a precision of about 2%, which is consistent with good industry practice[27]. Emissions associated with operating pumps, compressors, or other ancillary equipment at the injection site are to be reported as part of the injection system. Although not specified in the guidelines, these emissions could be estimated based on fuel consumption. Perhaps most important are the injection wells themselves, which may be a conduit for releases to the atmosphere, both during the injection phase of the project as well after injection stops and the wells are plugged and abandoned[28,29]. IPCC Guidelines include monitoring and reporting these emissions from wells as part of the geological storage system.

Geological Reservoir System

The final system in the capture and storage system chain is the geological storage reservoir itself. Potential storage formations include oil and gas reservoirs (either as part of an EOR/EGR operation or in an inactive depleted reservoir), so-called saline formations (brine-filled porous reservoirs) and deep unminable coal formations (including the possibility of CO_2-enhanced methane recovery)[4]. Under IPCC inventory guidelines, like the other components of the CCS chain, the geological reservoir is considered as a source of emissions. From an inventory perspective, the system boundary is therefore, the interface between the land surface and the atmosphere, or in the case of sub-sea bed storage, between the seabed and the overlying water column[26]. Any CO_2 emissions, originating from the geological storage reservoir, that cross these boundaries should be attributed to the geological storage system.

It is important to highlight that from an inventory perspective, migration out of the storage reservoir that does not reach the land surface or seabed is not considered to be an emission. This is one of important distinctions between monitoring of the purpose of inventory verification and monitoring for the purpose of health, safety and environmental concerns. Whereas detecting that CO_2 has migrated into an aquifer would be needed to assess health and safety risks, it is not in and of itself needed for inventory verification. Thus, the focus of the monitoring programs could be quite different from these two perspectives.

Of the 4 components of the CCS system, the least experience is available for assessing and monitoring CO_2 emissions from geological storage reservoir. Therefore, the following paragraphs will summarize what is known about retention rates and potential emissions.

Retention Rates and Expected Emissions from Geological Storage Reservoirs

Worldwide, generally accepted performance standards regarding the retention rates, or leakage rates, from geological storage reservoirs have not been established. In Australia, the CO2CRC is proposing retention rates of 99% over 1000 years[30]. Hepple and Benson[31] concluded that if leakage rates were less than 0.01%/year (equivalent to 90% retention over 1000 years), geological storage would be very effective as a greenhouse gas mitigation method. Others have suggested that somewhat less stringent requirements would provide sufficient benefits to warrant widespread application of CCS[32,33]. The IPCC Special Report concluded that at least 99% retention is likely for well selected and managed storage sites[4].

While this discussion highlights that there is not a consensus on the performance standards for geological storage reservoirs, it is fair to say that geological storage sites are expected to have very high retention rates and will be selected to provide essentially permanent storage of injected CO_2. However, not all storage projects will perform perfectly and it is to be expected that occasionally an abandoned well will leak. However, if detected, leaks from abandoned wells can be stopped and as will be discussed shortly, methods are available to identify such occurrences. In some cases, the reservoir seal may not be adequately characterized, limiting the amount of CO_2 that can be stored or rendering the site unsuitable for storage. In the worst case, the injected CO_2 could be removed from the reservoir and stored elsewhere.

There is growing consensus that the highest risk of leakage will occur during the injection phase of the project or shortly thereafter, perhaps over the next several decades. Support for this conclusion comes from a number of perspectives.

First, reservoir pressures will be highest during the active injection phase of the project, thus the driving forces that could cause leakage will be greatest during this time. For example, if the capillary entry pressure of the seal is exceeded allowing CO_2 penetration through the seal, this is most likely to occur during injection. Similarly, the possibility for fault reactivation is greatest while the reservoir pressure is high. Potential leakage rates through wells are also likely to highest while the reservoir pressure is high. Furthermore, wells found to leak will be plugged, thus decreasing the risk of future leakage.

Second, after injection stops, physical and chemical processes begin to immobilize and further trap CO_2. Carbon dioxide will continue to dissolve in the formation fluids, imbibition of brine will trap CO_2 by capillary forces and over longer time periods, CO_2 can be converted to minerals[4,34,35,36]. Once these processes immobilize the CO_2, even if the well construction materials continue to degrade, the probability of leakage is lower than during the injection phase of the project.

Finally, during the injection phase of the project, ongoing monitoring can be used to calibrate and refine the model of the reservoir, including migration rates and pathways, thus providing a high degree of confidence by the time injection stops. Post-injection monitoring can be used to gain further confidence, including providing an assessment of the rates of dissolution, capillary and mineral trapping.

One the basis of these considerations and the newness of CCS technology, IPCC inventory guidelines conclude that there is not enough information to establish default emission factors for geological storage reservoirs[26]. Instead, guidelines recommend the following 4-step procedure for determining emissions from the geological storage system[26].

1. Properly and thoroughly characterize the geology of the storage site and surrounding strata;

2. Model the injection of CO_2 into the storage reservoir and the future behavior;
3. Monitor the storage system; and
4. Use the monitoring results to validate or update the model.

Due to large geological variability between prospective storage sites, specific methods for monitoring are not proposed. Instead, the inventory compiler needs to assure that the monitoring plan is adequate, and in particular, focused on the areas where emissions are most likely to occur (e.g. wells and faults).

Annual reporting of emissions from the geological storage system is expected. In years where no direct monitoring data is available, validated models can be used to estimate emissions. Annual reports are expected to include the information provided in Table 1. The approach outlined in ref. 26 provides a high degree of flexibility with regard to the monitoring and modeling methods that are deployed. Specifications for detection limits and accuracy are not provided.

Annual Reporting for Inventory Accounting From the Geological Storage System
Mass of CO_2 injected during the reporting year
Mass stored during the reporting year
Cumulative mass stored in the geological storage system
Sources of CO_2, including infrastructure along the CCS chain
Report on monitoring rationale and methodology
Report on update to models
Mass of fugitive emissions to the atmosphere or sea bed during the reporting year
Description of the monitoring program, including frequency and results
Results of third party verification of the monitoring program and methods

Table 1. Annual reporting requirements for inventory verification (from ref. 26).

Information Needed for Carbon Credit Trading

Implementation of CCS on a wide scale is likely to take place in the context of a carbon credit trading regime or with development of low-emission portfolio standards where the value of emission reductions can be monetized. Today, the estimated cost of CCS of \$20 to \$70 per tonne of CO_2 avoided, and commensurate increase in electrical generation costs of 1 to 5 cents per kW-hr, make it unlikely to be implemented without financial incentives, such as those provided by trading schemes or portfolio standards[4]. Only in a limited number of cases where CO_2-EOR is combined with CCS is it economically favorably today.

Potential vehicles for providing financial incentives to CCS include the European Union Emissions Trading System, and under the Kyoto Protocol, the Clean Development Mechanism (CDM) and Joint Implementation (JI). To date, there are no CCS projects approved under these mechanisms. However, two CDM methodologies for CCS have been proposed and are under discussion at this time.

There are a number of issues that arise in the context of CCS and carbon credit trading, including but not limited to project boundaries, permanence and monitoring. Specific issues include: accounting and responsibility for emissions to the atmosphere or seabed; responsibility for monitoring during and after the crediting period; methodology for site selection; monitoring methods and periodicity; and dealing with unexpected accidents. This paper will address issues specifically related to monitoring, and its relationship to permanence.

The inventory verification approach described above provides a reasonable model framework for carbon credit trading. In particular, CCS can be treated as an emission reduction, measured at the point of generation (e.g. power plant or gas processing facility). Credit for emission reductions can then be decreased by the amount of CO_2 emitted from the pipeline system, the injection system, and the geological storage reservoir system.

Treating the geological storage reservoir as an emission source has a distinct advantage insofar as emissions will be easier to measure than underground storage inventories. It is worth spending a moment exploring this idea more fully.

When CO_2 is injected into a geological storage reservoir, some fraction of if remains as a separate phase, some dissolves into or mixes with the in situ formation fluids (oil or water), and some is converted to minerals. The distribution of these phases will vary spatially and temporally. In addition, density of separate phase CO_2 will vary depending on the pressure and temperature, again changing as a function of space and time. As a result of the complex, spatially and temporally varying distribution of CO_2, quantifying the *in situ* inventory will be difficult. Moreover, seismic imaging methods, which are presently the most effective approach for monitoring the location of CO_2 in the subsurface, are not particularly sensitive to the saturation of CO_2, once it exceeds several percent of the pore space[37]. The precision of methods for monitoring the *in situ* inventory of CO_2 have not been systematically assessed, however, based on the arguments provided above, it is unlikely that precision of greater than ±20% will be possible, even under the best of circumstances. Therefore, monitoring migration out of the storage reservoir and emissions to the surface are a more precise and reliable methods for verifying CO_2 storage.

The major question then becomes, how are emissions from the geological storage reservoir determined, and with what level of detection and precision? One possibility is to apply an emission factor, similar to the emission factors that are used for pipelines. However, this approach has several drawbacks.

First, there is not a long track record from which to assess emission factors. However, if one were to determine an geological storage reservoir emission factor today based on the experience at Sleipner, In Salah and Weyburn, it would be zero, as no emissions have been detected for any of these projects[12,14,38]. Second, the risk-profile for every geological storage system will differ based on its geological attributes and manmade structures (e.g. wells). For example, in mature oilfields, emissions are most likely to result from leakage through active and abandoned wells. For "Greenfield" saline formations, the largest risk may result from incomplete knowledge of the reservoir seal. Coalbeds may experience large pressure changes that could influence the geomechanical integrity of the coalbeds. Assigning an emission factor to estimate emissions from the geological storage reservoir would not appropriately recognize these differences.

Finally, there has been a tendency to use information about leakage and retention rates in the literature in ways that it was not intended to be used (e.g. ref. 4, 31-33). For example, Hepple and Benson[31], concluded that for leakage rates of less than 10^{-4} of the cumulative amount stored, geological storage would be highly effective as a greenhouse gas mitigation technique. This work and others like it did not suggest that geological storage reservoirs would actually leak at these rates. Similarly, the IPCC Special Report on CO_2 Capture and Storage concluded that it is likely that 99% of the CO_2 would be retained over 1000 years[4]. However, it did not conclude that 1% was likely to leak out over the same period. These studies were never intended to be used for assigning emission factors from geological storage reservoirs, and they should not be used as such.

In summary, the framework provided by the inventory accounting methodology in ref. 26 is an effective model for monitoring and verification of CCS in a carbon credit trading regime. Determining emission reductions from the point of generation (capture and compression), and emissions from pipelines and the injection system are comparatively straightforward. Methods for monitoring and verifying emissions from the geological storage reservoir are needed. At this time, the most appropriate approach is measure them, in contrast to using default emission factors. The following discussion addresses issues regarding methods and detection levels.

Background Fluxes of CO_2 in Natural Ecosystems and Emissions from Geological Storage Reservoirs

Distinguishing emissions from a geological storage reservoir from background emissions is the biggest challenge for measuring emissions from a geological storage reservoir. Everywhere, CO_2 is continuously exchanged between the land surface and the atmosphere. Each year about 300 billion tonnes of CO_2 are taken up by photosynthesis and a nearly equal amount is released by respiration and decomposition of organic matter. Fluxes vary widely from place to place, from day to night and over the seasons. Figure 2 provides an example of these fluxes from a forested site at Willow Creek in Wisconsin[40]. As shown, during late autumn and the cold winter months, CO_2 fluxes are small, on the order of ±30 $\mu g/m^2/s$. Once spring begins, fluxes increase dramatically, with large uptake by plants during the day and releases at night. During periods of active photosynthesis, peak fluxes can be on the order of ± several thousand $\mu g/m^2/s$. On balance, over the course of this year, this site is a net sink for CO_2, accumulating 25 $\mu g/m^2/s$ in the forest ecosystem.

Figure 3 shows a data set from a very different setting, the arctic tundra at Barrow Island in Alaska. These data collected during the growing season of 2002 show much smaller fluxes. Daytime uptake is significantly greater than releases from respiration at night during the growing season. Comparison between these two data sets demonstrates the large variability between sites. Consequently, any monitoring program focused on direct measurement of emissions from a geological storage site must obtain site specific baseline data. It also illustrates the complexity of attributing emissions to a geological storage reservoir in the presence of fluctuating background fluxes. In essence, emissions from the storage reservoir would need to be on the same order of magnitude or greater to detect them.

These data sets were collected using the eddy-covariance method which relies on a combination of wind velocity and CO_2 concentration measurements[41]. These data indicate that the resolution of these instruments is on the order of 10 $\mu g/m^2/s$. Miles (Ref. 23) concluded that emissions of about 45 $\mu g/m^2/s$ could be distinguished from natural background fluxes.

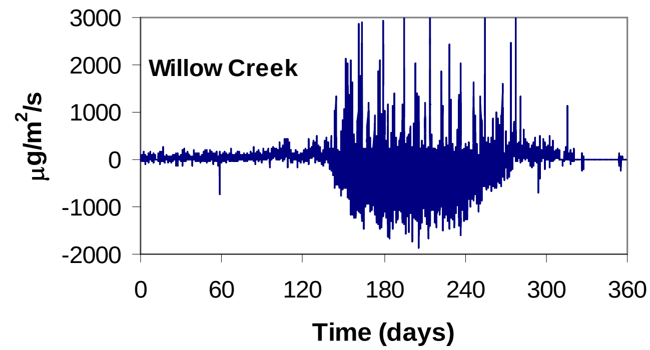

Figure 2. Annual CO_2 emissions measured every one-half hour from the Willow Creek site in Wisconsin during 2005. Data provided courtesy of Ken Davis and Paul Bolstad through the CDIAC Data Archive of the Ameriflux data[39]. Day 1 is January 1, 2005.

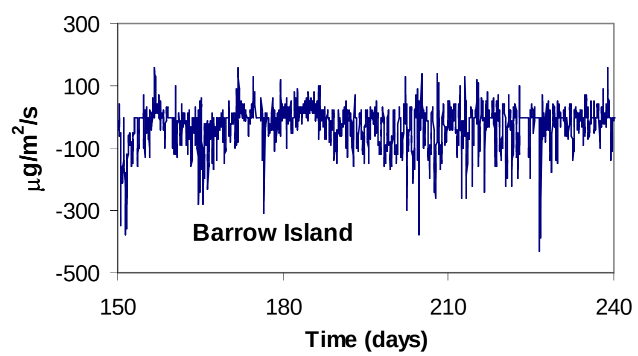

Figure 3. Annual CO_2 emissions measured every one-half hour from the Barrow Island site in Alaska. Data provided courtesy of Walter Oechel of San Diego State University through the CDIAC Data Archive of the Ameriflux data[40]. Day 1 is January 1, 2002.

Spatial and Temporal Distribution of CO_2 Emissions from Geological Storage Reservoirs

While CO_2 storage reservoirs are not intended or expected to leak, it is also worth considering the nature of emissions from a CO_2 storage reservoir if they did occur. Two factors are important, namely, how they would vary over time and the spatial pattern of the emission on the land surface. Not having actual experience with CO_2 releases from geological storage reservoirs, it is necessary to speculate on both counts. However, numerical simulations and observations from hydrocarbon and CO_2 emissions from natural reservoirs provide insight into both of these.

First, with regard to the spatial distribution of emissions, there are two primary pathways that are most likely to cause leakage, wells and faults. Consequently, emissions from either of these sources are likely to be confined to a small area in comparison to the overall size of the geological storage reservoir and CO_2 plume. Geochemical exploration data shown in Figure 4 from the Pineview Oilfield obtained in mid-1970 demonstrates this conclusion well. Soil gas samples with elevated C1-C4 concentrations correlate with location of faults and are confined to a small fraction of the footprint of the oilfield.

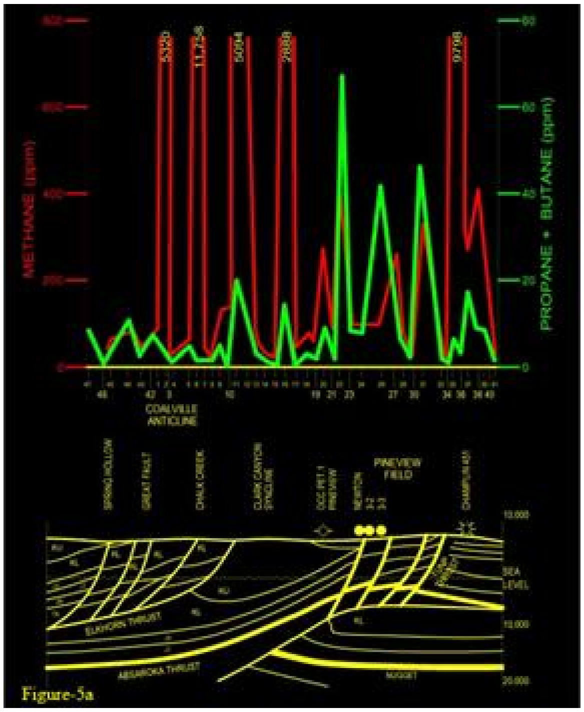

Figure 4. Illustration showing the relationship between faults and elevated C1-C4 concentrations from the Pineview Oilfield (from ref. 42).

Emissions from leaking wells would also be expected to be confined to a comparatively small surface area. Depending on the nature of the leak, CO_2 could either migrate directly up high permeability pathways caused by incompletely sealed well, or, could be diverted laterally into shallower secondary traps. In the former case, emissions would be confined to the area around the leaking well itself. In the later, emissions may be distributed somewhat more broadly, but again, would be confined to a small fraction of the plume.

The conclusion that emissions will be confined to a small fraction of the footprint of the plume is also supported by vadose zone transport simulations [43]. For leakage rates ranging over 3 orders of magnitude, in spite of the fact that CO_2 is roughly twice as dense as air at atmospheric pressures, vadose zone transport of CO_2 was essentially vertical, with relatively little lateral spreading. Consequently, surface emissions would be largely confined to the area directly above the location where CO_2 migrates into the vadose zone from below.

With regard to the second factor, that is, temporal variations in emissions, we can also draw inference from simulations and analogues. Simulations have shown that leakage up a fault is controlled by both self enhancing and self-limiting processes, but during the early stages of migration, the rate of leakage would be expected to increase monotonically as brine is displaced by CO_2[44,45]. Eventually emission rates would be expected to stabilize as an interconnected pathway is established between the storage reservoir and the surface. Once an interconnected pathway is established, fluctuations resulting from the interplay of self-enhancing and self-limiting processes may create cyclical variations in emission rates, but the period of these fluctuations is likely to be longer than the daily fluctuations typical of ecosystems. A schematic illustrating these two possibilities is shown in Figure 5. Small daily to weekly variations in emissions due to fluctuations in barometric pressure and soil moisture would also be superimposed on these emissions[46].

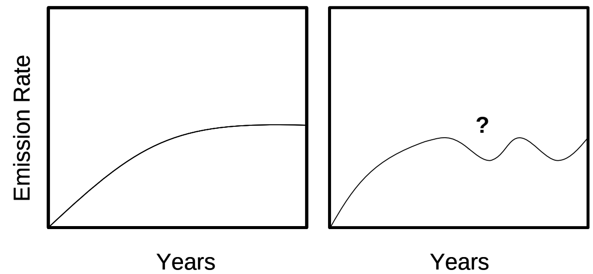

Figure 5. Schematic illustrating how emissions from a leaking fault may evolve over time.

Temporal variations in emission rates from leaking wells would depend on the nature of leak. If the leak occurs through the inside of the well casing, leakage rates may fluctuate rapidly, cycling through rapid discharges (e.g. Crystal Geyser[47]) followed by quiescent periods while the well refills with water and CO_2. Alternatively, if CO_2 migrates up the annulus of the well casing, emissions are likely to be stable, first increasing with time then approaching a nearly stable value as the brine saturation along the leakage pathway stabilizes.

Combined Emissions Above a Geological Storage Reservoir

The combination of emissions from natural ecosystem fluxes and the geological storage reservoir will result in the superposition of these two different sources of emissions. Averaged over a large area (e.g. the extent of the geological storage reservoir), to first order, the total emissions will simply be the sum of the two sources. However, directly where emissions occur, feedback between natural ecosystem fluxes and emissions from the storage reservoir would be expected. At low concentrations, increases in CO_2 can stimulate plant growth, which would increase uptake of CO_2. Conversely, as soil gas compositions increase to 10% or more, vegetation can become stressed or die, thereby decreasing CO_2 uptake. If the "flux footprint" of the emission monitoring system is large compared to the footprint of the emissions from the geological storage reservoir, these feedbacks should not have a significant affect on the measured emission rates? If however, the "flux footprint" of the monitoring system is on the same order as the emission footprint from the geological storage reservoir, these feedbacks may influence measured rates and should be considered in the evaluation of emission data.

Emissions from industrial sources such as power plants, refineries, and cement plants may also be significant in the vicinity of a storage project. In this case, baseline emissions from these sources should also be well characterized prior to starting the storage project. Since O_2 and CO_2 are stochiometrically anti-correlated for combustion sources, O_2 measurements may be useful for distinguishing industrial sources of CO_2 from emissions from geological storage reservoirs.

Detection Limits and Quantification of Emissions from Geological Storage Reservoirs

Defining the detection limit and the precision of measurements is necessary for developing an appropriate monitoring program. If detection limits and precision are not established, the quality of national GHG inventories and the value of carbon credits uncertain. If the detection limit is too high, it could compromise the effectiveness of CCS, provide inaccurate greenhouse gas inventories, and not provide the needed assurances for carbon credit trading. If the required detection limit is too low, the cost of implementing the monitoring program would be unnecessarily high, thus discouraging widespread implementation of CCS. To date, criteria for establishing these have not been developed. Here, we explore a number of approaches, and the strengths and weaknesses of them.

Options for Determining Detection Limits

We can now identify a number of approaches for determining the appropriate detection limit for measuring emissions from a geological storage reservoir. Some options, including examples of detection limits, and the benefits and drawbacks of each approach, are summarized in Table 2. For example, it has been suggested that the detection limit be based on some fraction of the background fluxes. This approach has the advantage the detection limit could be large compared to the background flux, thus providing some assurance that the emissions above this level could be detected. However, in areas with very large background fluxes, this approach may not provide a sufficiently stringent detection level to assure that CCS is effective as a GHG mitigation technique. Alternatively, the detection limit could be tied to the leakage rate that would assure the effectiveness of CCS. But, depending on the size of the storage project, especially for small ones, detecting very small emissions may be too challenging for the technology available today.

To determine which among these approaches may be most effective, it is worth considering the attributes that are most important in designing an approach to setting detection limits. Clearly, the following are important:

1. Simple, both with regard to explaining and implementing the approach;
2. Defensible, in terms of being sufficiently stringent to ensure that geological storage will be effective as a GHG mitigation technique;
3. Verifiable, in that the underlying measurements are reliable and the value of carbon credits can be assigned with confidence and certainty.

Of the options listed in Table 2, the approach that is closest to meeting all of these criteria is Option 3: detecting a specified emission from the geological storage reservoir per year (e.g. 1,000, 5,000, or 10,000 tonnes per year). However, each approach has strengths and weaknesses that must be considered before any approach is finally adopted. In the following section, Option 3 is explored in greater depth.

Application to a Hypothetical Storage Project

To further explore the utility of this approach, let us examine how it would be applied to a hypothetical geological storage project. Assume a 50 year project where 4 Mt per year of CO_2 (approximately equivalent to a 500 MW coal-fired power plant with CCS) are stored in a 1,500 m deep geological reservoir. Over 50 years, a total of 200 Mt of CO_2 would eventually be injected underground. For the reservoir properties listed in Table 3 the footprint of the CO_2 plume will occupy an area of about 130 km^2 at the end of the injection period.

The first question—is the detection limit simple to understand and implement? Clearly it is simple to understand and explain. For example, emissions from the geological storage reservoir should be monitored with a detection limit of 5,000 tonnes per year (or other appropriate value). That is, if emissions are lower than this, they are considered to be below detection and negligible. If greater, emissions are detectable and the quantity measured would be considered as a source of CO_2 that would be deducted from emission reductions at the generating source (e.g. power plant). With regard to implementation, administratively this is also simple, as described above. More will be said later about the practicality of designing and implementing a monitoring system which could detect a specified quantity of CO_2 emissions per year, such as from 1,000 to 10,000 tonnes per year.

The second question—is the approach defensible with regard to the effectiveness of CCS as a greenhouse gas mitigation technique? Clearly, the answer to this will depend on the specific value assigned as the detection limit. But more generally the question is, if emissions occur at or below the detection limit, will they be so high as to render CCS ineffective as a greenhouse gas mitigation technique? We can address this for our specific example. First, we will focus on the operational period. Over 50 years, 200 Mt of CO_2 will be stored. Fig. 6 provides an example of leakage rates (quantified in terms of the annual leakage as a percentage of the total amount stored) that would be detectable for emission detection limits of 1,000, 5,000 and 10,000 tonnes per year. As shown, for all of these detection limits, leakage rates of 0.01%/year or lower would be eventually be quantifiable using this approach. For a detection limit of 1,000 tonnes per year this occurs within the first few years of monitoring, for detection limits of 5,000 and 10,000 tonnes per year it may take a decade or longer. Nevertheless, detection limits in the range of 1,000 to 10,000 tonnes per year would be sufficiently sensitive to demonstrate that the geological storage is an effective GHG mitigation technique.

Method for Establishing Detection Limits	Example Detection Limits	Benefits	Drawbacks
Fraction of background CO_2 flux	50% of the average annual flux	Relates detection limits to a site specific baseline, increasing the probability that it can be detected	Natural fluxes vary from place to place, so the detection limit would be different for each storage site No apriori assurance that the metric would be sufficiently stringent
Percent of the CO_2 that will be injected into the storage reservoir	0.01%/year of the expected maximum storage quantity	Provides a single metric from which the effectiveness of all storage project can be assessed	May be challenging to meet for very small projects where only a small amount is stored
Specified CO_2 emission per year	5,000 tonnes per year	Simple and easy to understand	Large projects would be held to a higher overall performance standard than smaller projects
Prescribed CO_2 flux	50 $\mu g/m^2/s$	Single standard that would apply to all sites	Complex, may be difficult to distinguish based on background variability
Instrument- based method	10 $\mu g/m^2/s$ using eddy covariance towers	Well defined metric tied to measured detection limits	Changes in technology over time would make detection limits a moving target May be too sensitive to distinguish from background fluxes

Table 2. Options for quantifying detection limits for emissions from a geological storage reservoir.

The third question is—can emissions of this magnitude be measured and distinguished from other natural or industrial CO_2 fluxes reliably? There are two ways to address this question. First, what are the magnitudes of the natural and industrial emissions compared to a detection limit of 1,000, 5,000 or 10,000 tonnes per year? And second, are there measurement approaches that can reliably detect and quantify these emissions? The next section of this paper addresses the second question. Here we simply answer the question about the comparative size of the natural background and hypothetical emissions from the geological storage reservoir. We can use the data provided in Figures 2 and 3 to inform our hypothetical case study. Table 4 summarizes how the average annual flux (measured in $\mu g/m^2/s$) would change as a result of adding the emissions from the geological storage reservoir to the natural fluxes at the Willow Creek site. Five different footprints for the CO_2 emissions are considered, 100% of the plume (e.g. 130 km^2), 25%, 10%, 5% and 1%. At the Willow Creek Site the average baseline emission was -25.2$\mu g/m^2/s$ (e.g. the site is a net sink for CO_2). As shown, if the flux is distributed over the entire extent of the plume, detection and quantification would be challenging. For smaller emission footprints of 10% or less, large changes in average annual fluxes are evident, and the land surface changes from a sink to a source of CO_2. For emission footprint of 10% or less, detection and quantification should be readily achievable. In addition to comparing average fluxes, it is also possible to consider how the fluxes would change over the year.

Storage Reservoir Properties for the Hypothetical Example
Annual Injection Rate: 5 Mt/year Project Duration: 50 years Reservoir Thickness: 100 m In Situ CO_2 Density: 600 kg/m^3 Porosity: 25% Average CO_2 Pore Volume Occupancy: 10%

Table 3. Storage reservoir properties for the hypothetical example.

During winter months, average baseline fluxes are about ±30 ($\mu g/m^2/s$). For emission footprints of 10% or less, the increase in CO_2 flux would be directly measurable for 5,000 and 10,000 tonnes per year detection limits. For 1,000 tonnes per year, the emission footprint would need to be 2.5% or less to be directly detectable from wintertime flux measurements. Lower background fluxes during the winter months make emission detection more favorable during time of the year. A reconnaissance program focused on leak detection should obtain measurements during this time of the year.

The effect of large industrial point sources on the ability to quantify emissions geological storage reservoirs should also be considered, but is not done here.

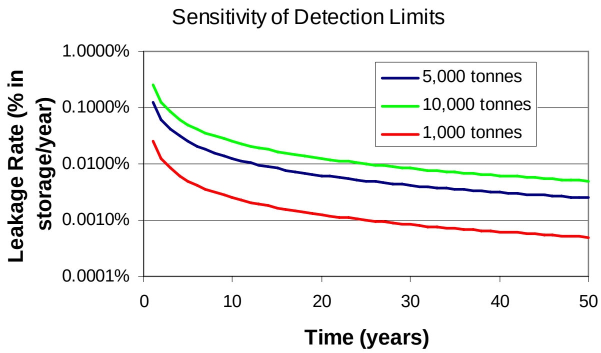

Figure 6. Sensitivity of leakage rate quantification to detection limits.

	Average Annual CO_2 Fluxes ($\mu g/m^2/s$)				
	Footprint of CO_2 Emissions Sources as a Fraction of the Plume Footprint				
Emission Rate (tonnes/year)	100%	25%	10%	5%	1%
1,000	-25.0	-24.2	-22.8	-20.3	-0.8
5,000	-24.0	-20.3	-13.0	-0.80	96.8
10,000	-22.8	-15.4	-0.80	23.6	219

Table 4. Average annual emissions calculated from the sum of the natural fluxes (from the Willow Creek Site) and hypothetical emissions of 1,000, 5,000 and 10,000 tonnes/year. The average annual baseline flux is -25.2 $\mu g/m^2/s$ for Willow Creek.

Monitoring Approaches and Technologies

Numerous studies have compiled and evaluated technologies for monitoring CO_2 storage projects[9,11,14,49,50]. They demonstrate that the toolbox of monitoring methods is large and provide reasonable assurance that the location of the CO_2 plume can be tracked using 4-D seismic imaging, and CO_2 fluxes can be quantified using eddy covariance towers or flux accumulation chambers. Other studies demonstrate that the cost of monitoring is comparatively small (undiscounted life cycle monitoring costs on the order of \$0.1 to \$0.30 per tonne of CO_2)[9].The purpose of the discussion here is to lay out the comparative benefits and drawbacks of different monitoring strategies for the purpose of inventory verification and carbon credits.

Figure 7 illustrates components of the subsurface system and the opportunities they present for monitoring. For example, for on-shore geological storage reservoirs, monitoring for leakage can take place in the storage reservoir itself, in shallow saline formations that contain secondary accumulations of CO_2, as dissolved and secondary accumulations in groundwater, CO_2 in vadose zone gas, terrestrial ecosystems and finally by monitoring direct emissions into the atmosphere. While leaking faults and fractures (indicated by sub-vertical white lines in the diagram) would also contain CO_2, detection is likely to be difficult here as a result of their comparatively small size and unfavorable geometry[50]. For off-shore storage reservoirs, the deeper components of the system are the same as their on-shore counterparts. However, as CO_2 approaches the seabed, the physical environment, ecosystems and monitoring approaches are quite different. Dissolution into sea-water, transport with the water column and discharge at the sea-air interface present special monitoring challenges. Table 5 summarizes the methods, benefits and drawbacks for monitoring each of these components of the system in the context of inventory verification and carbon credit trading.

As indicated by the information in Table 5, there are a large number of approaches and options for monitoring emissions from geological storage reservoirs. Today, the most practical and cost-effective approach would rely on a combination of measurements and model predictions to assess annual emissions from the geological storage reservoir. Since the same combination of measurements would not be appropriate for all storage sites, flexibility to tailor the monitoring to the specific geological attributes of the storage site would be beneficial.

For example, if a storage reservoir is overlain by a saline formation beneath a secondary seal, pressure monitoring and seismic imaging can be extremely effective for detecting migration out of the storage reservoir, particularly near known vulnerabilities such as abandoned wells or faults. Figure 8 provides a schematic of showing how pressure monitoring could be used to provide early warning that a fault is leaking. Calculations of the pressure increases that would occur in the monitoring formation for the range of parameters listed in Fig. 8 indicate that readily measurable pressure changes (>0.007 bar) would occur within a year for leaking faults located within a kilometer of the injection well for a wide range of permeability (see Fig. 8). Similar calculations (not shown) for leakage around a well casing or up an abandoned well show similarly high sensitivity, with a high probability of detecting leakage on the order of 5,000 tonnes/year at distances of up to 1 km. Similarly, seismic monitoring of CO_2 that has migrated out of the storage reservoir and become trapped as a secondary accumulation is a promising option for some sites. Studies have shown that under some conditions, such as those at Sleipner, Weyburn and Frio Formation, TX, accumulations on the order of 1,000 to 10,000 tonnes can be detected at depths of a kilometer and accumulations as small as 100 tonnes could be detected at a depth of about 500 m[12,14,16,49,50]. Under these conditions it would be reasonable to conclude that if there is no CO_2 migration out of the storage reservoir, then there would be no emissions at the surface. Thus, a monitoring program which demonstrated containment within the storage reservoir should suffice as "proof" that there are no emissions from the storage reservoir. Accepting this as proof would require that the geological conditions are favorable for imaging secondary accumulations or detecting pressure buildup due to leakage. This could be assessed during pre-injection site characterization and permitting.

There are however conditions under which another monitoring strategy may be more effective. For example, if there are no secondary seals or permeable formations above the storage reservoir to monitor, this approach may not be effective. In this case, atmospheric and near-surface based monitoring may be the preferred approach. Again, careful consideration should be given to the design of the monitoring program. The primary purpose of a surface-based monitoring program should be to detect whether or not emissions are occurring. This can be done by focusing the monitoring program on known vulnerabilities such as abandoned wells, and surface expressions of faults and fractures. Looking for vegetative stress caused by elevated soil gas concentrations can provide quick reconnaissance of areas with potential leakage[25]. Plane-based or satellite based hyperspectral imaging can be used to locate areas where emissions are likely. Alternatively, direct visual observations could also be used to look for changes in vegetation or soils that may indicate emissions. If emissions are detected, the precise location can then be determined using flux chambers or soil gas monitoring. Once located, eddy covariance towers and/or flux accumulation chambers can used to quantify emission rates, with a detection limit as described previously.

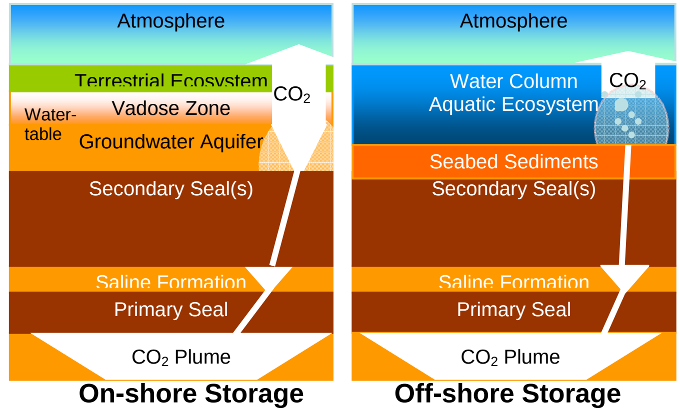

Figure 7. Schematic showing the components of the surface and how they may be used for monitoring.

System Component	Monitoring Methods	Benefits	Drawbacks
Storage reservoir	**Seismic** Gravity Well logs Fluid sampling	History match to calibrate and validate models Early warning of migration from the storage reservoir	Mass balance difficult to monitor Dissolved and mineralized CO_2 difficult to detect
Shallower saline formations below secondary seals	**Seismic** **Pressure** Gravity Well logs Fluid sampling	Good sensitivity to small secondary accumulations (~10^3 tonnes) and leakage rates Early warning of leakage	Detection difficult if secondary accumulations do not occur Dissolved and mineralized CO_2 difficult to detect
		On-shore	
Groundwater aquifers	**Seismic** **Pressure** **EM** Gravity SP Well logs Fluid sampling	Sensitivity to small secondary accumulations (~10^2-10^3 tonnes) and leakage rates More monitoring methods available Detection of dissolved CO_2 less costly with shallow wells	Detection after significant migration has occurred Detection after potential groundwater impacts have occurred
Vadose zone	**Soil gas and vadose zone sampling**	CO_2 accumulates in vadose zone making detection easier compared to atmospheric detection Early detection in vadose zone could trigger remediation before large emissions occur	Significant effort for null result (e.g. no CO_2 from storage detected) Detection only after some emissions are imminent Does not provide quantitative information on emission rate
Terrestrial ecosystems	**Vegetative stress**	Vegetative stress can be readily observed using routine observation Satellite and plane-based methods available for quick reconnaissance	Detection only after emissions have occurred Vegetative stress can be caused by other factors Land use change could alter the baseline Does not provide quantitative information on emission rates May not be useful in some ecosystems (e.g. deserts)
Atmosphere	**Eddy covariance** **Flux accumulation chamber** Optical methods	Good for quantification of emissions	Distinguishing storage emissions from natural ecosystem and industrial sources necessitates comprehensive monitoring May not be best suited for detecting anomalous emissions due to relatively small footprint compared to the size of the plume Significant effort for null result
		Offshore	
Water Column	Ship based fluid sampling and analysis Autonomous vehicles with CO_2, pH and carbon cycle sensors	Direct measurement of water column and fluxes (using inverse models)	Distinguishing storage related fluxes from natural variability comprehensive monitoring Quantifying separate phase CO_2 flux Significant effort for null result
Atmosphere	Optical methods Eddy covariance	Direct measurement of emission rate	Technology not well developed for this application Quantification of emissions may be impractical Changing emission footprint from ocean currents Likely to be costly to maintain Significant effort for null result

Table 5. Monitoring approaches and options for measuring emissions from geological storage formations. Methods in bold text are the best developed.

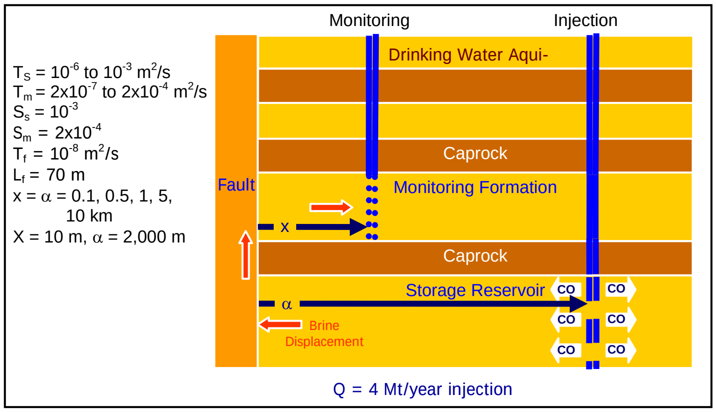

Figure 8. Schematic of pressure monitoring for leakage up a fault into an overlying saline formation used for monitoring.

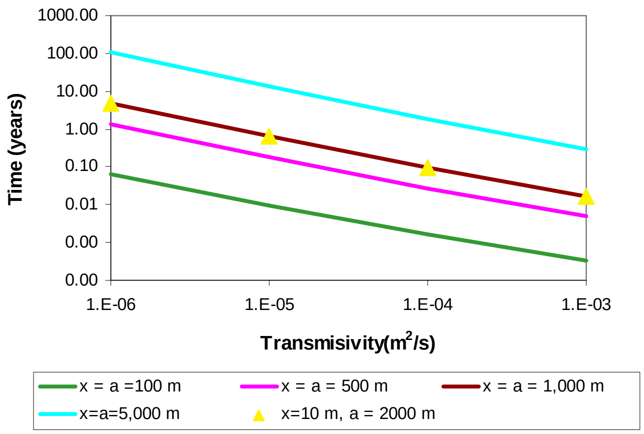

Figure 9. Time to have a 0.007 bar (0.1 psi) pressure buildup due to leakage up a fault for the parameters provided in Figure 8.

A common thread between surface-based and subsurface based monitoring approaches is the hierarchy to first detect, then locate and quantify emissions. Designing a monitoring program to continuously quantify emission rates is premature in light of the low expected emission rates. Moreover, in the unlikely event that emissions are detected, more reliable and precise data will be obtained from a system located in close proximity to the source of emissions and tailored to specific information about the size and cause of emissions.

Opportunities for Improvement

While the toolbox of monitoring techniques for assessing emissions from geological storage reservoirs is large, there is always room for improvement. In particular, the following actions and innovations would be helpful:

1. Obtain more experience with direct emission measurements by collecting data from existing CO_2-EOR projects.
2. Conduct controlled release experiments for demonstrating the ability to detect, locate and quantify emissions.
3. Develop innovative methods for measuring CO_2 concentrations and emissions on a spatial scale commensurate with geological storage projects. Optical techniques with path lengths on the order of 1 to 10 km would be very helpful in this regard.
4. Design deployment approaches that enhance the ability to distinguish natural ecosystem fluxes from emissions from a geological storage reservoir. Options include using natural (e.g. isotopes) or introduced tracers, configuring the detection system to avoid atmospheric mixing, and robust statistical approaches for deconvolving the emission signatures from various sources.
5. Advance the ability of geophysical and pressure monitoring approaches to detect small secondary accumulations of CO_2 and small rates of migration out of the storage reservoir.

A concerted effort to gain more experience measuring emissions, demonstrating reliability under controlled conditions, and technological innovation will increase confidence in inventory verification and the value of carbon credits from CCS.

Conclusions

While geological storage reservoirs are not intended or expected to leak, inventory accounting and carbon credit trading will require reliable methods for determining whether or not a geological storage reservoir is a source of CO_2 emissions into the atmosphere. New guidelines for inventory accounting have determined that geological storage reservoirs should be considered as a source of emissions, and that credit for emissions reductions should be taken as the difference between the emission reduction at the source and fugitive emissions from pipelines, the injection system and the geological storage reservoir. This same approach is useful for carbon credit trading.

Monitoring methods are available today that that can be used to detect, locate and quantify emissions. If emissions occur, the surface footprint of the emission is likely to be distributed over a small fraction of the footprint of the CO_2 plume in the geological storage reservoir. Consequently, even for very low emission rates, the fluxes are likely to be significantly higher than background fluxes associated with natural ecosystem processes. Should emissions occur, they can be detected from vegetative stress, changes in surface vegetation or a variety of techniques for directly measuring emissions.

It is important to establish a detection limit for monitoring emissions, below which emissions are considered to be negligible and below detection. A number of approaches for setting detection limits are provided, the simplest of which is to assign a specified annual emission (e.g. 1,000, 5,000, 10,000 tonnes/year) as the detection limit. However, determining the most effective approach is complex, and the benefits and drawbacks of the various approaches should be carefully considered before adopting an approach. Regardless of which approach is taken it must be:

- Simple, both with regard to explaining and implementing the approach;

- Defensible, in terms of being sufficiently stringent to ensure that geological storage will be effective as a GHG mitigation technique;
- Verifiable, in that the underlying measurements are reliable and the value of carbon credits can be assigned with confidence and certainty.

Choosing a detection limit should not be confused with assigning a default emission factor for a geological storage reservoir. In fact, if we were to choose a default emission factor today, it should be zero.

An effective monitoring program should focus first on detecting whether or not emissions are occurring, Once emissions, or the possibility for emissions are detected, a more intense effort can be made to precisely locate and quantify them. Designing a monitoring program in the first instance to quantify emission rates would be unnecessarily costly and, if emissions were to occur, unlikely to provide as reliable data as a tailored program would be.

Maintaining flexibility in the implementation approach is also important. For example, some sites are ideally suited for detecting minor amounts of CO_2 migration out of the geological storage reservoir into the overlying strata. Both seismic monitoring to detect small secondary accumulations (1,000 to 10,000 tonnes) and pressure monitoring to detect migration up wells or faults could be the sufficient to conclude that emissions are negligible. At other sites, such as those without secondary seals, a direct surface-based emissions monitoring program may be more appropriate. Additionally, differences between off-shore and on-shore monitoring constraints are likely to influence the choice of monitoring system, as direct emission measurements will be more challenging in off-shore settings. In this case, a greater reliance on geophysical imaging (e.g. seismic, pressure and gravity) is appropriate.

Looking to the future, a concerted effort to gain more experience measuring emissions, demonstrating reliability under controlled conditions, and technological innovation will further increase confidence in inventory verification and the value of carbon credits from CCS.

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